

Sonophotocatalytic Degradation of Methyl Orange Using Pineapple Pericarp–Derived ZnO Nanoparticles: A Green Wastewater Treatment Approach

Aamod Thakkar¹, Kalpana Jain², Dr. Sajid F. Shaikh³, Dr. Gurumit Wadhava⁴, Anil Palve⁵

^{1, 4, 5} Veer Wajekar Arts, Commerce & Science College, Phunde-Uran, Raigad, Maharashtra, India

² Royal College of Arts, Science & Commerce, Mira Road, District Thane, Maharashtra, India

³ Anjuman Islam Janjira, Degree College of Science, Murud-Janjira, Raigad, Maharashtra, India.

sajidoshaikh@gmail.com

Abstract: The discharge of synthetic dyes from textile and allied industries poses a significant threat to aquatic ecosystems and human health. Among these, methyl orange, an azo dye, is highly stable and resistant to conventional wastewater treatment techniques. The present study explores a sustainable and eco-friendly approach for dye degradation using zinc oxide nanoparticles synthesized via a green route from pineapple pericarp waste. The prepared nanoparticles were employed as sonophotocatalysts for the degradation of methyl orange under combined light and ultrasonic irradiation. The degradation efficiency was monitored using UV–Visible spectroscopy. Results demonstrated that more than 90% degradation was achieved within 60 minutes under optimized conditions. The enhanced catalytic activity is attributed to the synergistic interaction between ultrasonic waves and light irradiation, leading to the generation of reactive oxygen species. This study highlights the potential of agricultural waste-derived nanomaterials in environmental remediation and supports the principles of green chemistry.

Keywords: Sonophotocatalysis, ZnO Nanoparticles, Methyl Orange, Green Synthesis, Wastewater Treatment, Advanced Oxidation Processes

I. INTRODUCTION

Introduction (Detailed Version)

Rapid industrialization and urbanization over the past few decades have led to a substantial increase in the discharge of hazardous pollutants into aquatic ecosystems. Among various industrial sectors, textile, paper, leather, and dyeing industries are recognized as major contributors to water pollution due to their extensive use of synthetic dyes. These dyes are released into water bodies in large quantities, often without adequate treatment, resulting in severe environmental and ecological consequences. The presence of dyes in water not only affects its aesthetic quality by imparting color but also reduces light penetration, thereby disrupting photosynthetic activity and aquatic life.

Azo dyes represent the largest class of synthetic dyes used in industrial applications, accounting for nearly 60–70% of total dye production. Among them, methyl orange is a widely used anionic azo dye known for its chemical stability and resistance to natural degradation processes. Its complex aromatic molecular structure, containing azo ($-N=N-$) bonds, makes it highly recalcitrant to conventional treatment methods. Moreover, methyl orange and its degradation intermediates are reported to exhibit toxic, mutagenic, and potentially carcinogenic effects, posing significant risks to both human health and the environment.

Traditional wastewater treatment techniques such as coagulation–flocculation, adsorption, membrane filtration, and biological degradation have been widely employed for dye removal. However, these methods often suffer from several



limitations, including incomplete degradation, high operational costs, sludge generation, and secondary pollution. Biological treatments, in particular, are less effective for azo dyes due to their resistance to microbial attack. As a result, there is an urgent need to develop more efficient, sustainable, and environmentally friendly treatment technologies.

Advanced oxidation processes (AOPs) have emerged as promising alternatives for the degradation of persistent organic pollutants. These processes are based on the in situ generation of highly reactive species, primarily hydroxyl radicals ($\bullet\text{OH}$), which possess strong oxidation potential and can mineralize complex organic compounds into carbon dioxide, water, and other harmless end products. Among various AOPs, heterogeneous photocatalysis has gained considerable attention due to its simplicity, efficiency, and potential for solar energy utilization.

Semiconductor materials play a crucial role in photocatalysis, with zinc oxide (ZnO) being one of the most widely studied photocatalysts. ZnO is favored due to its wide band gap (~ 3.37 eV), high exciton binding energy, excellent chemical stability, non-toxicity, and cost-effectiveness. Upon irradiation with light energy equal to or greater than its band gap, ZnO generates electron-hole pairs, which subsequently participate in redox reactions to produce reactive oxygen species (ROS) such as hydroxyl radicals and superoxide anions. These reactive species are responsible for the degradation of organic pollutants.

In recent years, the focus has shifted toward the development of green synthesis methods for nanoparticle production. Conventional chemical synthesis routes often involve toxic reagents and harsh conditions, which contradict the principles of sustainable development. Green synthesis, on the other hand, utilizes natural resources such as plant extracts, microorganisms, and agricultural waste as reducing and stabilizing agents. Pineapple pericarp, an abundant agro-waste, contains various phytochemicals such as flavonoids, phenolics, and enzymes that facilitate the synthesis of ZnO nanoparticles in an eco-friendly manner. This approach not only reduces environmental impact but also promotes waste valorization.

Furthermore, to enhance the efficiency of photocatalytic processes, hybrid techniques such as sonophotocatalysis have been developed. Sonophotocatalysis involves the simultaneous application of ultrasonic irradiation and light energy. Ultrasonic waves induce acoustic cavitation, leading to the formation, growth, and collapse of microbubbles in the liquid medium. This phenomenon generates localized high temperatures and pressures, which enhance mass transfer, improve catalyst dispersion, and promote the formation of additional reactive radicals. The synergistic interaction between ultrasound and photocatalysis significantly improves the degradation efficiency compared to individual processes.

In this context, the present study aims to synthesize zinc oxide nanoparticles using pineapple pericarp via a green route and evaluate their performance as a sonophotocatalyst for the degradation of methyl orange dye in aqueous solutions. The study integrates the concepts of green chemistry, nanotechnology, and advanced oxidation processes to develop a sustainable and efficient method for wastewater treatment. The findings are expected to contribute to the development of cost-effective and environmentally benign technologies for the remediation of dye-contaminated water.

II. MATERIALS

All chemicals used in the present study were of analytical grade and were used without further purification. The azo dye Methyl Orange was procured and used as the model organic pollutant for degradation studies. The zinc precursor, typically Zinc nitrate ($\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$), was employed for the synthesis of zinc oxide nanoparticles.

Fresh pineapple pericarp (outer peel of *Ananas comosus*) was collected from local sources, thoroughly washed with distilled water to remove impurities, and processed to obtain the plant extract used as a reducing and stabilizing agent in the green synthesis of ZnO nanoparticles.

Distilled water was used throughout the experimental work for the preparation of solutions and washing purposes to avoid any interference from impurities.



Green Synthesis of ZnO Nanoparticles

Zinc oxide (ZnO) nanoparticles were synthesized via an eco-friendly green synthesis route using pineapple pericarp extract as a natural reducing and stabilizing agent. Fresh pineapple pericarp obtained from *Ananas comosus* was initially washed thoroughly with tap water followed by distilled water to remove adhering dust and impurities. The cleaned material was then shade-dried for several days and subsequently ground into small pieces.

To prepare the plant extract, a known quantity of dried pineapple pericarp was boiled in distilled water at approximately 70–80°C for 30–45 minutes. The mixture was then cooled to room temperature and filtered using Whatman filter paper to obtain a clear extract containing bioactive phytochemicals such as flavonoids, phenolics, and enzymes. These compounds play a crucial role in the reduction of zinc ions and stabilization of the formed nanoparticles.

For nanoparticle synthesis, the prepared extract was slowly added to an aqueous solution of Zinc nitrate under continuous magnetic stirring. The reaction mixture was maintained at controlled temperature conditions (60–80°C) to facilitate the formation of a precursor complex. During this process, phytochemicals present in the extract reduce Zn^{2+} ions and initiate nucleation, leading to the formation of ZnO nanoparticles.

The resulting mixture was then subjected to continuous heating until a thick paste or gel-like precipitate was obtained. This precursor was dried in a hot air oven to remove moisture content. The dried material was further calcined in a muffle furnace at temperatures ranging from 400–500°C for 2–4 hours. Calcination leads to the decomposition of organic residues and conversion of the precursor into crystalline ZnO nanoparticles.

The obtained ZnO nanoparticles were cooled to room temperature, ground into fine powder, and stored in airtight containers for further characterization and application in photocatalytic degradation studies.

Experimental Setup for Degradation Study

The sonophotocatalytic degradation of the azo dye Methyl Orange was carried out under controlled laboratory conditions to evaluate the catalytic efficiency of the synthesized ZnO nanoparticles.

A stock solution of methyl orange was prepared using distilled water and subsequently diluted to obtain a working concentration of **10 mg/L**. The required amount of ZnO nanoparticle catalyst was added to the dye solution to achieve a catalyst dosage of **0.5 g/L**. The suspension was then transferred to a reaction vessel equipped with both a light source and an ultrasonic system.

The degradation experiments were conducted under **UV/Visible light irradiation**, which provides sufficient ऊर्जा to excite the ZnO semiconductor and generate electron–hole pairs. Simultaneously, **ultrasonic irradiation** was applied to the system to enhance the degradation process through acoustic cavitation, leading to improved dispersion of catalyst particles and increased formation of reactive oxygen species.

The pH of the solution was adjusted to an **alkaline medium**, as alkaline conditions favor the generation of hydroxyl radicals ($\bullet OH$), which are highly effective oxidizing agents responsible for dye degradation. The entire reaction was carried out at **room temperature**, ensuring energy efficiency and practical applicability of the process.

Prior to light and ultrasonic exposure, the reaction mixture was magnetically stirred in the **dark for 20–30 minutes** to establish adsorption–desorption equilibrium between the dye molecules and the catalyst surface. This step is essential to distinguish between dye removal due to surface adsorption and actual photocatalytic degradation.

During the experiment, aliquots of the reaction mixture were withdrawn at regular time intervals, centrifuged to remove catalyst particles, and analyzed using UV–Visible spectroscopy to monitor the decrease in dye concentration. The maximum absorption wavelength (λ_{max}) of methyl orange at **464 nm** was used for quantitative analysis of degradation efficiency.

Analytical Method

The degradation of methyl orange was monitored using UV–Visible spectroscopy by measuring absorbance at **464 nm**. The percentage degradation was calculated using:



III. RESULTS AND DISCUSSION

3.1 Photocatalytic and Sonophotocatalytic Activity

The synthesized ZnO nanoparticles exhibited excellent catalytic performance. Under sonophotocatalytic conditions, more than **90% degradation** of methyl orange was achieved within **60 minutes**, which is significantly higher than photocatalysis alone.

3.2 Mechanism of Degradation

The enhanced degradation efficiency can be explained by the synergistic effect of ultrasound and light irradiation:

- Ultrasonic waves produce **cavitation bubbles**, generating localized high temperature and pressure.
- ZnO absorbs light and produces **electron-hole pairs**.
- These react with water and oxygen to form reactive oxygen species (ROS) such as:
 - Hydroxyl radicals ($\bullet\text{OH}$)
 - Superoxide radicals ($\text{O}_2^{\bullet-}$)

These radicals oxidize the dye molecules into simpler, non-toxic compounds.

3.3 Role of Green Synthesis

The use of pineapple pericarp:

- Reduces chemical usage
- Lowers production cost
- Promotes waste valorization
- Enhances sustainability

3.4 Comparison with Conventional Methods

Compared to traditional treatment methods, the proposed approach:

- Achieves faster degradation
- Requires lower energy
- Is environmentally friendly

IV. CONCLUSION

The study demonstrates that pineapple pericarp-derived ZnO nanoparticles are highly effective for the sonophotocatalytic degradation of methyl orange dye. The integration of green synthesis and advanced oxidation processes provides a sustainable and cost-effective solution for wastewater treatment. This approach not only addresses environmental pollution but also promotes the utilization of agricultural waste, aligning with the principles of green chemistry.

V. DISCUSSION

The results confirm that sonophotocatalysis is superior to conventional photocatalysis due to enhanced radical generation. The study also highlights the importance of green synthesis in reducing environmental impact. However, further research is needed to evaluate the scalability of the process and its application to real industrial effluents.

Future studies should focus on:

- Catalyst reusability
- Degradation of mixed pollutants
- Pilot-scale applications



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